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(A) Hair care composition containing modified aminoalkyl substituted polydiorganosiloxane.

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- Proprietor: DOW CORNING CORPORATION 3901 S. Saginaw Road Midland Michigan 48686-0995(US)
- Inventor: Kohl, Gretchen Sutton 1308 Bookness Midland, MI(US) Inventor: Lane, Thomas Howard 107 Varner Court Midland, MI(US)
- Representative: Laredo, Jack Joseph et al Elkington and Fife Prospect House 8 Pembroke Road Sevenoaks, Kent TN13 1XR(GB)

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Description

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This invention relates to the use of modified aminoalkyl substituted polydiorganosiloxane in hair care compositions such as conditioners and shampoos. More specifically, the invention relates to compositions and methods for treating hair with polydiorganosiloxane containing aminoalkyl groups modified by alkoxycarbonylalkyl substituents.

Aminoalkyl substituted polydiorganosiloxanes are well known copolymers which are typically composed of dimethylsiloxane units and aminoalkylmethylsiloxane units. For example, Starch, U.S. Patent No. 4,563,347, January 7, 1986, describes a copolymer represented by the formula

$$\begin{array}{c} (\mathrm{CH_3})_3 \mathrm{Sio} (\mathrm{CH_3}_3 \mathrm{Sio})_2 [(\mathrm{CH_3})_2 \mathrm{Sio}]_{96} \mathrm{Si} (\mathrm{CH_3})_3 \\ \mathrm{CH_2CH} (\mathrm{CH_3}) \mathrm{CH_2NHCH_2CH_2NH_2} \end{array} .$$

Such copolymers are further described in the CTFA Cosmetic Ingredient Dictionary, 3rd edition, 1982, published by The Cosmetic, Toiletry and Fragrance Association, Inc., 1133 Fifteenth Street NW Washington D.C. (USA) under the nomenclature amodimethicone and trimethylsilylamodimethicone.

DE-A-2621460 describes the treatment of various wool and other keratinous fibers such as mohair, cashmere and alpaca to render them resistant to shrinkage on laundering and/or to impart thereto other desirable properties such as improved handle (softness) and resistance to pilling. The treatment composition comprises (A) a polydiorganosiloxane having a molecular weight of at least 2500 and terminal -OX radicals wherein X represents a hydrogen atom or an alkyl or alkoxyalkyl radical having up to 15 carbon atoms, at least two of the silicon-bonded substituents present in said polydiorganosiloxane being monovalent radicals composed of carbon, hydrogen, nitrogen and, optionally, oxygen, which radicals contain at least two amine groups and are attached to silicon through a silicon to carbon linkage, and at lest 50 percent of the total silicon-bonded substituents in said polydiorganosiloxane being methyl radicals, any remaining substituents being monovalent hydrocarbon radicals having from 2 to 20 inclusive carbon atoms, and (B) an organosiloxane having at least three silicon-bonded hydrogen atoms in the molecule and in which the organic radicals are alkyl radicals having less than 19 carbon atoms.

The use of aminoalkyl substituted polydiorganosiloxane in hair care compositions is also well known. For instance, Starch, U.S. Patent No. 4,563,347, teaches using these copolymers in hair conditioning compositions to improve combing and feel characteristics. Similarly, Grollier et al., UK Patent Application Nos. 2,157,168 and 2,143,434, October 23, 1985 and February 13, 1985 respectively, teach using the aminoalkyl substituted polydiorganosiloxanes with other components in hair care compositions which may be formulated as a shampoo, a rinsed or non-rinsed lotion, a restructuring composition, a composition for blow drying or a composition for permanent waving.

The aminoalkyl substituents are credited with providing the copolymers with cationic sites that make the polymer more substantive to hair than nonsubstituted polydimethylsiloxane. However, the chemical reactivity of the aminoalkyl groups may also present a problem in regard to compatibility with other common components of hair care formulations. Compatibility problems may be observed especially with anionic surfactants. Tangney et al., U.S. Patent No. 4,507,455 March 26, 1985, describe a method of modifying the chemical reactivity of aminoalkyl substituents of polydiorganosiloxane by reacting the polymer with a monocarboxylic acid anhydride to acylate the amine groups and thus convert them to amides. While acylation was effective to improve compatibility, it has also been found to reduce the substantivity of the polymer to hair so that the utility of the polymers in hair care compositions is limited. It is a purpose of the present invention to provide hair care compositions containing a conditioning silicone polymer which has the advantage of being highly substantive to hair but at the same time has a more moderate chemical reactivity with correspondingly reduced compatibility problems.

Aminoalkyl substituted silanes and polydiorganosiloxanes have been reacted With acrylate esters to provide silanes and polydiorganosiloxanes in which the amine is modified by addition of an alkoxycar-bonylalkyl group to the nitrogen atom. For example, the reaction is illustrated as follows for methylacrylate addition to an aminopropyl substituent of a polydiorganosiloxane.

More specifically, Pike et al., U.S. Patent No. 3,033,815,. May 8, 1962, describe the reaction of

methylacrylate with a silicone copolymer of 90 percent dimethylsiloxane units and 10 percent deltaaminobutylmethylsiloxane units. The resulting silicone is described as containing delta-(N-2-carbomethoxyethyl)aminobutylmethylsiloxane units. Pike et al. teach that these compounds find use as sizes for fibrous materials, particularly fibrous glass materials employed in combination with thermosetting resins and that the monomeric and polymeric compounds can also be employed as adhesives or as flocculation agents.

Similarly, Ryan, U.S. Patent No. 3,317,577, May 2, 1967, describes the addition of methylacrylat, to silanes and organosiloxanes having diaminoalkyl groups such as N-(2-amino ethyl)-3-aminopropyl groups (-CH₂CH₂CH₂CH₂CH₂CH₂). Ryan teaches that the materials are useful as binding agents for binding pigments to glass fabric and other siliceous surfaces, that they are useful as priming agents on metallic surfaces for securing adhesion of subsequently applied resin coatings, that they are useful as binding agents in the preparation of glass fiber polyester laminates, and that fluids prepared from the polymers and copolymers are also of interest as heat exchange agents and for further reaction to modify organic materials.

Neither Pike et al. nor Ryan suggest that their modified aminoalkyl substituted polydiorganosiloxanes are useful in hair care compositions. The use of these materials in hair treating compositions is believed to be novel.

The present invention relates to a composition for treating human hair comprising (a) from 0.01 to 10 parts by weight of an organopolysiloxane represented by the formula

 $XR_2SiO(RYSiO)_n(R_2SiO)_mSiR_2X$

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wherein R denotes a monovalent hydrocarbon radical having 1 to 6 carbon atoms;: X denotes -OH, -OR, Y, or R; Y denotes a substituent of the formula

$$-R^{1}N[(CH_{2})_{b}^{N}]_{p}CHR^{2}CHR^{3}COOR^{4}$$

wherein R¹ denotes an alkylene radical having 3 to 6 carbon atoms, R² denotes a hydrogen atom, phenyl, or an alkyl radical of 1 to 6 carbon atoms, R³ denotes a hydrogen atom or methyl radical, and R⁴ denotes an alkyl radical having 1 to 6 carbon atoms, b has a value of 2, 3, or 4, p has a value of 0, 1, or 2, and Q denotes a hydrogen atom or a radical of the formula -CHR²CHR³COOR⁴ wherein R², R³, and R⁴ have the same meanings as defined above; m has an average value from 40 to 600; n has an average value of 0 to 100 with the proviso that when n is 0, X denotes Y and (b) from 50 to 100 parts by weight of a physiologically acceptable carrier. The invention also relates to the method of conditioning human hair

In the present invention, certain modified aminoalkyl substituted polydiorganosiloxanes are used in compositions for treating human hair such as conditioners, rinses, and shampoos. The useful polydiorganosiloxanes are represented by the formula

which comprises contacting human hair with the treatment composition defined above.

 $XR_2SiO(RYSiO)_n(R_2SiO)_mSiR_2X$

wherein R denotes a monovalent hydrocarbon radical having 1 to 6 carbon atoms. The organic groups denoted by R in formula I may be alkyl groups such as methyl, ethyl, or hexyl; alkenyl groups such as vinyl or allyl; or an aryl group such as phenyl. The diorganosiloxane polymers most useful in this invention are predominantly methyl substituted polymers wherein at least 90 percent of R radicals in the formula are methyl groups. It is most preferred to use polydimethylsiloxanes wherein essentially all R radicals are methyl groups.

In formula I, X denotes -OH, -OR, Y, or R where R has the same meaning described above and Y denotes a modified aminoalkyl substituent. Thus, the polymer may be terminated by a hydroxyl group, a hydrocarbonoxy group, or a triorganosiloxane unit. When n is not zero so that the polymer has pendant modified aminoalkyl substituents, it is preferred that the polymer be terminated by triorganosiloxane units such as dimethylvinylsiloxane units, dimethylphenylsiloxane units or trimethylsiloxane units, with trimethylsiloxane units being most preferred. When n is zero, X denotes a modified aminoalkyl substituent so that useful polymers have the formula

YR₂SiO(R₂SiO)_mSiR₂Y

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wherein R has the same meaning as described above.

In formula I and II. Y denotes a modified aminoalkyl substituent represented by the formula

wherein R¹ denotes an alkylene radical having 3 to 6 carbon atoms. Alkylene radical, R¹, may be a straight chain radical such as trimethylene, tetramethylene, or hexamethylene or a branched radical such as 2-methylpropylene, -CH₂CH(CH₃)CH₂-. R² denotes a hydrogen atom, phenyl, or an alkyl radical of 1 to 6 carbon atoms such as methyl, isopropyl, butyl, or hexyl. R³ denotes a hydrogen atom of a methyl radical. R⁴ denotes an alkyl radical having 1 to 6 carbon atoms, for example, methyl, ethyl, propyl, pentyl, or isobutyl. In the modified aminoalkyl substituent, b may have a value of 2, 3, or 4 and p may have a value of 0, 1, or 2. Q denotes a hydrogen atom, an alkyl radical having 1 to 4 carbon atoms, or a radical of the formula -CHR²CHR³COOR⁴ wherein R², R³, and R⁴ have the same meanings as defined previously. Alkyl radicals having 1 to 4 carbon atoms include methyl, ethyl, isopropyl and butyl. Generally, silicones are preferred wherein Q denotes a hydrogen atom or a radical of the formula -CHR²CHR³COOR⁴.

According to the present invention, useful modified aminoalkyl substituents include, for example,

 $- \text{CH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{COOCH}_3, \quad - \text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{COOCH}_3, \quad - \text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{COOCH}_3, \quad - \text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{COOCH}_2\text{CH}_3, \quad - \text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{COOCH}_2\text{CH}_3, \quad - \text{CH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{COOCH}_3)_2, \quad - \text{CH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{N(CH}_2\text{COOCH}_3)_2, \quad - \text{CH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{N(CH}_2\text{COOCH}_3)_2, \quad - \text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{N(CH}_2\text{COOCH}_3)_2, \quad - \text{CH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{N(CH}_2\text{COOCH}_3)_2, \quad - \text{CH}_2\text{CH}_2\text{N(CH}_2\text{CH}_2\text{N(CH}_2\text{COOCH}_3)_2, \quad - \text{CH}_2\text{CH}_2\text{N(CH}_2\text{COOCH}_3)_2, \quad - \text{CH}_2\text{CH}_2\text{N(CH}_2\text{COOCH}_3)_2, \quad - \text{CH}_2\text{CH}_2\text{N(CH}_2\text{CH}_2\text{N(CH}_2\text{COOCH}_3)_2, \quad - \text{CH}_2\text{CH}_2\text{N(CH}_2\text{CH}_2\text{N(CH}_2\text{COOCH}_3)_2, \quad - \text{CH}_2\text{CH}_2\text{N(CH}_2\text{COOCH}_3)_2, \quad - \text{CH}_2\text{CH}_2\text{N(CH}_2\text{CH}_2\text{N(CH}_2\text{COOCH}_3)_2, \quad - \text{CH}_2\text{CH}_2\text{N(CH}_2\text{CH}_2\text{N(CH}_2\text{CH}_2\text{COOCH}_3)_2, \quad - \text{CH}_2\text{CH}_2\text{N(CH}_2\text{CH}_2\text{N(CH}_2\text{COOCH}_3)_2, \quad - \text{CH}_2\text{CH}_2\text{N(CH}_2\text{CH}_2\text{N(CH}_2\text{COOCH}_3)_2, \quad - \text{CH}_2\text{CH}_2\text{N(CH}_2\text{CH}_2\text{N(CH}_2\text{COOCH}_3)_2, \quad - \text{CH}_2\text{CH}_2\text{N(CH}_2\text{COOCH}_3)_2, \quad - \text{CH}_2\text{CH}_2\text{N(CH}_2\text{CH}_2\text{COOCH}_3)_2, \quad - \text{CH}_2\text{CH}_2\text{N(CH}_2\text{CH}_2\text{COOCH}_3)_2, \quad - \text{CH}_2\text{CH}_2\text{N(CH}_2\text{CH}_2\text{COOCH}_3)_2, \quad - \text{CH}_2\text{CH}_2\text{N(CH}_2\text{CH}_2\text{COOCH}_3)_2, \quad - \text{CH}_2\text{CH}_2\text{CH}_2\text{N(CH}_2\text{COOCH}_3)_2, \quad - \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N(CH}_2\text{CH}_2\text{COOCH}_3)_2, \quad - \text{CH}_2\text$

$$\begin{array}{c} -\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{COOCH}_2\text{CH}_3)_2, \\ \text{CH}_2\text{CH}_2\text{COOCH}_2\text{CH}_3 \end{array}$$

 $-CH_2CH_1CH_3CH_2NHCH_2CH_2NHCH_2CH_2NHCH_2CH_2COOCH_3, -CH_2CH_2CH_2NHCH_2CH(CH3)COOCH_3, \text{ and } -CH_2CH_2CH_2NH(CH_2)_3NHCH(C_6H_5)CH_2COOCH_2.$

The modified aminoalkyl substituted polydiorganosiloxane may vary widely in viscosity and degree of polymerization. In formula I, for example, m may vary from an average value of 40 to 600 and n may vary from an average value of 0 to 100. However, polymers wherein m has an average value from 40 to 400 and n has an average value from 1 to 60 with the ratio of n to m being less than or equal to 0.15 are generally preferred for use in the composition for treating human hair of this invention. Such polymers are preferred because they have viscosities which allow more easy formulation with other components typically used in hair treating compositions and because they have sufficient amino functionality to provide substantivity to hair

Methods of preparing the modified aminoalkyl substituted polydiorganosiloxanes that are employed in the composition for treating human hair according to this invention are known in the art. For example, U.S. Patent Nos. 3,033,815 and 3,317,577 teach methods whereby aminoalkyl substituted polydimethylsiloxanes are reacted with acrylate esters to prepare polymers useful in the present invention.

The modified aminoalkyl substituted polydiorganosiloxane must be dissolved or dispersed in a carrier to be useful for treating hair. Typically, useful hair treatment compositions will contain from 0.01 to 10 parts of silicone polymer diluted in 50 to 100 parts of a carrier liquid. Since the carrier serves only to dilute the silicone polymer to allow uniform application of appropriately small quantities, any carrier that is physiologically acceptable for use on the human body may be used. For example, the silicone polymer can be dissolved in organic solvents including chlorinated alkanes such as 1,1,1-trichloroethane and methylene dichloride, alcohols such as ethanol and isopropanol, and polyols such as ethylene glycol and propylene glycol.

The silicone polymer can also be used to treat human hair in an aqueous dispersion or emulsion. Treating hair with an emulsion of silicone in water is as especially preferred embodiment of the present invention. Aqueous emulsions of silicone polymer may be prepared by high shear mixing of the polymer in water using a suitable emulsifying surfactant as is well known in the art. Microemulsions of silicone

polymers in water are also highly preferred for use in the present invention. Microemulsions of modified aminoalkyl substituted polydiorganosiloxane can be prepared by the method described in U.S. Patent No. 4,620,878 which describes generally the preparation of emulsions of silicones containing polar substituents.

Depending on the specific hair treating application, the compositions of this invention may be thickened or unthickened creams, gels, aerosol foams, or sprays. Suitable thickeners include, among others, sodium alginate, gum arabic, polyoxyethylene, cellulose derivatives such as methylcellulose, hydroxymethylcellulose, hydroxypropylcellulose, hydroxypropylmethylcellulose, guar gum or its derivatives, starch and starch derivatives such as hydroxyethylamylose and starch amylose, locust bean gum, electrolytes such as NaCl, saccharides such as fructose and glucose, and derivatives of saccharides such as PEG-120 methyl glucose dioleate. The compositions for treating human hair may be applied in the form of shampoo; rinsing products to be applied after shampooing, before or after tinting or bleaching, and before or after permanent waving or straightening; products for setting or brushing; conditioning compositions, restoring compositions; and compositions for permanent-waved hair.

The types of compositions for treating human hair encompassed by the present invention is further illustrated, but not limited, by specific reference to the following preferred embodiments. Hair treating compositions of this invention may form a shampoo, in which case, the compositions contain a cleansing surfactant in addition to the silicone polymer and carrier. The concentration of cleansing surfactant can range from about 2 to 40 parts by weight per 100 parts of total composition. Cleansing surfactants selected from the group consisting of anionic surfactants, nonionic surfactants, and amphoteric surfactants are well known for use in shampoo formulations. For example, the anionic, nonionic and amphoteric surfactants useful as cleansing agents in shampoos are further described in U.S. Patent No. 4,559,227.

Typical cleansing surfactants include the anionics such as the sodium, ammonium, or triethanolamine salts of lauryl sulfate and lauryl ether sulfate; the nonionics such as fatty acid alkanolamides like lauric acid diethanolamide; and the amphoterics such as N-cocamidopropyl dimethyl glycine. Generally the anionic surfactants, especially the sodium, ammonium, and triethanolamine salts of lauryl sulfate, are preferred since they provide richer, denser foams than other types of cleansing surfactants at comparable concentrations.

In another embodiment of the present invention, the composition for treating human hair may form a conditioning product for application to hair after shampooing. The hair is typically rinsed in running water after treating with the conditioning product. Conditioners facilitate combing out hair and impart softness and suppleness to the hair. Conditioning products may also contain other components such as thickeners and auxiliary conditioning compounds. Auxiliary conditioning agents may be used to provide further improved conditioning benefits such as antistatic characteristics. Auxiliary conditioning agents useful in the compositions of this invention include the organic cationic compounds and polymers such as stearyldimethylbenzylammonium chloride, quaternary nitrogen derivatives of cellulose ethers, and homopolymers and copolymers of dimethyldiallylammonium chloride, and other quaternary ammonium compounds which are known for use in hair conditioning formulations.

In another embodiment of the present invention, the composition for treating human hair may be in the form of a product for permanent waving hair. The conventional technique for these permanent waves consists in applying, in a first stage, a composition containing a reducing agent and then, after having rinsed the hair if appropriate applying a composition containing an oxidizing agent. According to the present invention, at least one of the two compositions is a hair treating composition containing modified aminoalkyl substituted polydiorganosiloxane and carrier in addition to the reducing or oxidizing agent.

One advantage of the hair treating compositions of this invention is the increased amount of silicone polymer deposited on the hair in comparison to the amount of silicone deposited when hair is treated by prior art silicone materials. Also, the hair treating compositions of the invention are more easily formulated with other hair care components because of the reduced reactivity of the modified aminoalkyl substituted polydiorganosiloxane with other components.

The following examples are presented to illustrate the invention to those skilled in the art and should not be construed as limiting the invention, which is properly delineated in the appended claims. All proportions by parts or percents are by weight unless otherwise stated.

Example 1

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This example shows that aminoalkyl substituted polydiorganosiloxane which has been modified by reaction with methylacrylate is useful to condition hair. Also, the combing improvement provided by the methylacrylate modified silicone is compared to the improvement provided by the unmodified silicone and to silicone modified by reaction with acetic anhydride.

Hair treating compositions suitable for use as hair conditioners were prepared by making an emulsion of the various silicone polymers in water. Stock emulsions were prepared by mixing 4.4 g of isolaureth-6 (C₁₂H₂₅(OCH₂CH₂)₆OH sold under the trademark TERGITOL TMN-6 by Union Carbide Corp., Danbury, CT). 12.1 g of octoxynol-40 (C₈H₁₇C₆H₄(OCH₂CH₂)₄₀OH sold under the trademark TRITON X-405 by Rohm and Haas Company. Inc., Philadelphia, PA), and 76.1 g of water and then adding 50 g of silicone polymer while homogenizing the mixture on a colloid mill. Th stock emulsions contained 35% silicone, 11.6% emulsifying surfactants, and 53.4% water. Portions of each stock emulsion were diluted to 0.25% silicone with additional water to provide baths for treating hair in the following tests.

The silicone polymers tested generally conformed to the average formula

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$$(CH_3)_3$$
Sio $[CH_3]_2$ [$(CH_3)_2$ Sio $]_{96}$ Si $(CH_3)_3$.

The specific structure of the Y substituents for the polymers in each emulsion tested is shown in Table 1. Silicone Emulsions A and B illustrate the present invention while Silicone Emulsions C, D, and E represent the prior art and are presented for comparison purposes.

TABLE 1

	Silicone Emulsion	<u>¥</u>
25	A	-CH2CH(CH3)CH2NHCH2CH2NHCH2CH2COCH3
	B*	-CH ₂ CH(CH ₃)CH ₂ NCH ₂ CH ₂ CH ₂ CH ₂ COOCH ₃ Q Q
30	С	-CH ₂ CH(CH ₃)CH ₂ NHCH ₂ CH ₂ NH ₂
35	D.	-CH ₂ CH(CH ₃)CH ₂ NHCH ₂ CH ₂ NHCCH ₃
40	E	-CH ₂ CH(CH ₃)CH ₂ NCH ₂ CH ₂ NHCCH ₃ 0=CCH ₃

* Q groups are half hydrogen and half methoxycarbonylethyl groups of the formula -CH2CH2COOCH3

The conditioning efficacy of each silicone emulsion was evaluated by measuring the force required to comb both wet and dry hair after it had been treated with the compositions. Hair tresses were made by assembling 12 g bundles of 30 cm natural brown, virgin European hair and binding the root ends in wax. All reported combing results are averages for three tresses treated with each composition.

Combing forces were measured on an INSTRON strain gauge adapted with a hard rubber comb. The combing force was recorded as the comb was moved down through the tress which was attached to the end of a stationary load cell. The average combing load (ACL) was determined by integrating the total combing force over the entire tress length and is reported in grams. Four combing strokes were conducted for each treatment condition of a tress and averaged to obtain more representative values.

Tresses were washed with a conventional shampoo and dried at least 18 hr under ambient conditions prior to initial combing force measurement in the dry/untreated state. Tresses were then soaked in water for 12-30 minutes and combing forces measured again in the wet/untreated state. Between each of the four wet

combing strokes, the hair was dipped three times in water to uniformly retangle the hair. Tresses were then treated by dipping for 30 sec. in a 200 g bath of silicone emulsion (0.25% silicone solids). The tresses were rinsed for 30 sec. in 40°C. running tap water and the combing forces measured in the wet/treated state. Combing forces were measured again in the dry/treated state after the hair had dried for at least 18 hr under ambient conditions. Combs were changed between treated and untreated tresses, and a new comb is used for each treatment material.

The percent change in ACL was calculated as

where ACL_T is the average combing load for the treated tress and ACL_U is the average combing load for the untreated tress. Percent change values are shown in table 2 for both the dry and the wet state.

TABLE 2

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Silicone Emulsion Percent Change in ACL Treatment Dry Wet -37 -69 Α В -35 -53 С -65 -66 D -35 -63 Ε -10 +1

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Example 2

This example shows an additional type of methylacrylate modified aminoalkyl substituted polydiorganosiloxane that is useful to condition human hair. Also, the combing improvement provided by the methylacrylate modified silicone is compared to the improvement provided by the unmodified silicone.

Hair treating compositions were prepared by making an emulsion of the various silicone polymers in water according to the procedure described in Example 1. The silicone polymers tested generally conformed to the average formula

$(CH_3)_3$ Sio $[CH_3Sio]_2[(CH_3)_2$ Sio $]_{96}$ Si $(CH_3)_3$.

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The specific structure of the Y substituents for the polymers in each emulsion tested is shown in Table 3. Silicone Emulsion F illustrates the present invention while Silicone Emulsions G and H represent the prior art and are presented for comparison purposes.

TABLE 3

Silicone Emulsion	Y
F	-CH ₂ CH(CH ₃)CH ₂ N(CH ₃)CH ₂ CH ₂ COOCH ₃
G	-CH ₂ CH(CH ₃)CH ₂ NHCH ₃
. Н	-CH₂CH(CH₃)CH₂NHCH₂CH₂NH₂

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The conditioning efficacy of each silicone emulsion was evaluated by measuring the force required to comb dry hair after it had been treated with the compositions. The hair tresses were treated and combing forces measured by the same procedures described in Example 1. The percent change in average combing load between treated and untreated tresses is shown in Table 4.

TABLE 4

Silicone Emulsion Treatment	Percent Change in ACL
	Dry
F	-15
G	-52
Н	-12

Example 3

This example demonstrates the substantivity of the silicones of this invention on human hair and compares their substantivity to that of prior silicones used in hair care.

Clippings of the treated hair tresses from Example 1 were analyzed to determine the amount of silicone bound or adsorbed on the hair. In addition, after initial clippings were removed, the tresses were washed with 0.6 g of conventional shampoo for 60 sec., blow dried, and additional clippings taken for analysis. Additional washing steps were performed with further clippings taken for analysis after the 3rd and 5th wash.

Hair clippings were analyzed by atomic absorption determination of silicon after the hair had been digested with papain enzyme. The digested hair samples were extracted in acidified methyl isobutyl ketone for analysis. The results are presented as parts per million (ppm) of total silicon in Table 5.

The data in Table 5 demonstrates that the acrylate modified silicones surprisingly deposit more effectively on hair than the other materials, yet they are effectively removed after 1 to 3 washings so that undesirable build up on the hair does not occur.

Table 5

Silicone Treatment Silicon Detected (ppm) Number of Washes After Treatment В C* D* E* **Untreated Hair**

*Comparison examples, not encompassed by the present invention

Example 4

This example illustrates the preparation of a shampoo formulation within the hair treating compositions of the present invention. The shampoo employs ammonium lauryl sulfate as an anionic cleansing surfactant.

A shampoo was prepared by first heating a solution of 9 g of ammonium lauryl sulfate in 61 g of water to 80°C. A separate mixture of 6 g of lauric acid diethanolamide and 2 g of the silicone polymer from Silicone Emulsion A of Example 1 (a methylacrylate modified aminoalkyl substituted polydimethylsiloxane) was heated to 80°C. and then added with stirring to the agueous surfactant solution. A clear solution

resulted which was thickened by addition of 2.5 g of PEG-120 methyl glucose dioleate (a methyl glucoside derivative with two polyoxyethylene substituent groups containing a total of 120 oxyethylene units). The thickener was melted and then mixed into the shampoo composition. After cooling, the pH of the composition was adjusted to 6.8 with 25% aqueous citric acid solution and sufficient additional water added to make 100 g of shampoo composition.

Example 5

This example illustrates the preparation of a shampoo formulation within the hair treating compositions of the present invention. The shampoo employs a mixture of ammonium lauryl sulfate (anionic) and N-cocamidopropyl dimethyl glycine (amphoteric) as cleansing surfactant.

A mixture of 5.25 g of N-cocamidopropyl dimethyl glycine 4 g of lauric acid diethanolamide, 2 g of the silicone polymer from Silicone Emulsion A of Example 1, and 12.25 g of water was heated to 80 °C. and added to a similarly heated solution of 5.25 g of ammonium lauryl sulfate in 24.25 g of water. After cooling, an additional 43 g of water was added. The pH was adjusted to 5.5-6.0 with 25% aqueous citric acid. The solution was thickened by adding NaCl and sufficient additional water added to make 100 g of shampoo composition.

Example 6

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This example illustrates the improved skin toxicological characteristics of the silicones used in the hair treating compositions of the present invention. The silicone polymers described in Example 1 were tested for acute eye and dermal irritation in rabbits. The results are presented in Table 6.

25 Table 6

Silicone Polymer	Acute Eye Irritation	Acute Dermal Irritation
A B C* D* E*	slight irritant slight redness moderate irritant moderate irritant slight redness	slight irritant non-irritating moderate to severe irritation moderate irritation non-irritating

*Comparison examples, not encompassed by the present invention

Claims

A composition for treating human hair comprising

(a) from 0.01 to 10 parts by weight of a polydiorganosiloxane represented by the formula

 $XR_2SiO(RYSiO)_n(R_2SiO)_mSiR_2X$

wherein R denotes a monovalent hydrocarbon radical having 1 to 6 carbon atoms; X denotes -OH, -OR, Y, or R; Y denotes a substituent of the formula

$$-R^{1}$$
N[(CH₂)_bN]_pCHR²CHR³COOR⁴
Q Q

wherein R¹ denotes an alkylene radical having 3 to 6 carbon atoms, R² denotes a hydrogen atom, phenyl, or an alkyl radical of 1 to 6 carbon atoms, R³ denotes a hydrogen atom or methyl radical, and R⁴ denotes an alkyl radical having 1 to 6 carbon atoms, b has a value of 2, 3, or 4, p has a value of 0, 1, or 2, and Q denotes a hydrogen atom or a radical of the formula -CHR²CHR³COOR⁴ wherein R², R³, and R⁴ have the same meanings as defined above; m has an average value from 40

to 600; n has an average value of 0 to 100 with the proviso that when n is 0,X denotes Y, and (b) from 50 to 100 parts by weight of a physiologically acceptable carrier.

- 2. A hair treatment composition according to claim 1 wherein R denotes methyl and p has a value of 1.
- 3. A hair treatment composition according to claim 2 wherein X denotes methyl, n has an average value of 1 to 100, and Y denotes a substituent of the formula

$$-R^1$$
N(CH₂)₂NCH₂CHR³COOR⁴.

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4. A hair treatment composition according to claim 3 wherein the polydiorganosiloxane is represented by the formula

$$(CH_3)_3$$
SiO $[CH_3]_n$ $[(CH_3)_2$ SiO $]_m$ Si $(CH_3)_3$.

 CH_2 CH (CH_3) CH $_2$ NCH $_2$ CH $_2$ CH $_2$ COOR 4

A hair treatment composition according to claim 4 wherein the polydiorganosiloxane is represented by the formula

$$(CH_3)_3$$
SiO $[CH_3SiO]_n$ $[(CH_3)_2$ SiO $]_m$ Si $(CH_3)_3$.
 CH_2 CH (CH_3) CH $_2$ NHCH $_2$ CH $_2$ NHCH $_2$ CH $_2$ COOR 4

- 6. A hair treatment composition according to claim 4 wherein about 50 percent of the substituents denoted by Q are -CH₂CH₂COOR⁴ and the remainder are hydrogen.
- 40 7. A hair treatment composition according to claim 4 wherein the polydiorganosiloxane is represented by the formula

- 8. A hair treatment composition according to claim 4 wherein m has an average value from 40 to 400, n has an average value from 1 to 60, and ratio of n to m is less than or equal to 0.15.
 - 9. A hair treatment composition according to claim 8 wherein the carrier is water.

- 10. A hair treatment composition according to claim 1 which further comprises from 2 to 40 parts by weight of a cleansing surfactant selected from the group consisting of anionic surfactants, nonionic surfactants, and amphoteric surfactants.
- 11. A hair treatment composition according to claim 10 wherein the cleansing surfactant is an anionic surfactant.
 - 12. A hair treatment composition according to claim 11 wherein the anionic surfactant is a sodium, ammonium, or triethanolamine salt of laury! sulfate.
 - 13. A method of conditioning human hair which comprises contacting human hair with a composition as defined in any of claims 1 to 12.
 - 14. The use of a composition as defined in any of claims 1 to 12 to treat human hair.

Revendications

- Une composition pour le traitement des cheveux comprenant
 (a) 0,01 à 10 parties en poids d'un polydiorganosiloxane représenté par la formule
 - XR2SiO(RYSiO)n(R2SiO)mSiR2X
 - où R désigne un radical hydrocarboné monovalent ayant 1 à 6 atomes de carbone ; X désigne -OH, -OR, Y ou R ; Y désigne un substituant de la formule

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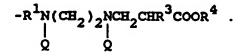
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où R¹ désigne un radical alkylène ayant 3 à 6 atomes de carbone, R² désigne un atome d'hydrogène, un radical phényle ou un radical alkyle de 1 à 6 atomes de carbone, R³ désigne un atome d'hydrogène ou un radical méthyle, et R⁴ désigne un radical alkyle ayant 1 à 6 atomes de carbone, la valeur de b est 2, 3 ou 4, la valeur de p est 0, 1 ou 2, et Q désigne un atome d'hydrogène ou un radical de la formule -CHR²CHR³COOR⁴ où R², R³ et R⁴ ont les mêmes significations que ci-dessus ; la valeur moyenne de m est de 40 à 600 ; la valeur moyenne de n est de 0 à 100, avec la condition que si n est 0, X désigne Y, et

- (b) 50 à 100 parties en poids d'un véhicule physiologiquement acceptable.
- Une composition de traitement des cheveux selon la revendication 1, dans laquelle R désigne un radical méthyle et la valeur de p est 1.
- 3. Une composition de traitement des cheveux selon la revendication 2, dans laquelle X désigne un radical méthyle, la valeur moyenne de n est de 1 à 100, et Y désigne un substituant de la formule



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 Une composition de traitement des cheveux selon la revendication 3, dans laquelle le polydiorganosiloxane est représenté par la formule

$$(CH_3)_3$$
sio $(CH_3sio)_n$ [$(CH_3)_2$ sio $)_m$ si $(CH_3)_3$.
 CH_2 CH (CH_3) CH $_2$ NCH $_2$ CH $_2$ CH $_2$ COOR 4

5. Une composition de traitement des cheveux selon la revendication 4, dans laquelle le polydiorganosiloxane est représenté par la formule

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$$(CH_3)_3$$
SiO $(CH_3$ SiO $)_n$ $(CH_3)_2$ SiO $)_m$ Si $(CH_3)_3$.
 CH_2 CH (CH_3) CH $_2$ NHCH $_2$ CH $_2$ NHCH $_2$ CH $_2$ COOR 4

- 6. Une composition de traitement des cheveux selon la revendication 4, dans laquelle environ 50 pour cent des substituants désignés par Q sont -CH₂CH₂COOR⁴ et ceux qui restent sont de l'hydrogène.
 - Une composition de traitement des cheveux selon la revendication 4, dans laquelle le polydiorganosiloxane est représenté par la formule

- 8. Une composition de traitement des cheveux selon la revendication 4, dans laquelle la valeur moyenne de m est de 40 à 400, la valeur moyenne de n est de 1 à 60, et le rapport de n à m est inférieur ou égal à 0,15.
- 40 9. Une composition de traitement des cheveux selon la revendication 8, dans laquelle le véhicule est l'eau.
 - 10. Une composition de traitement des cheveux selon la revendication 1, qui comprend, de plus, 2 à 40 parties en poids d'un agent tensio-actif nettoyant choisi dans le groupe formé par les agents tensio-actifs anioniques, les agents tensio-actifs non ioniques et les agents tensioactifs amphotères.
 - 11. Une composition de traitement des cheveux selon la revendication 10, dans laquelle l'agent tensio-actif nettoyant est un agent tensio-actif anionique.
- 12. Une composition de traitement des cheveux selon la revendication 11, dans laquelle l'agent tensio-actif anionique est un laurylsulfate de sodium, d'ammonium ou de triéthanolamine.
 - 13. Un procédé de conditionnement des cheveux qui consiste à mettre les cheveux en contact avec une composition telle que définie dans l'une quelconque des revendications 1 à 12.
 - 14. L'utilisation d'une composition telle que définie dans l'une quelconque des revendications 1 à 12 pour traiter des cheveux.

Patentansprüche

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1. Zusammensetzung zum Behandeln menschlichen Haares, enthaltend

(a) von 0,01-10 Gewichtsteile eines Polydiorganosiloxans der Formel $XR_2SiO(RYSiO)_n(R_2SiO)_mSiR_2X$, in der R eine einwertige Kohlenwasserstoffgruppe mit 1-6 Kohlenstoffatomen ist, X ist -OH, -OR, Y oder R und Y ist ein Substituent der Formel

$$-R^{1}N[(CH_{2})N]CHR^{2}CHR^{3}COOR^{4}$$
,

in der R¹ eine Alkylengruppe mit 3-6 Kohlenstoffatomen ist, R² ein Wasserstoffatom, Phenyl oder eine Alkylgruppe mit 1-6 Kohlenstoffatomen ist, R³ ist ein Wasserstoffatom oder eine Methylgruppe und R⁴ ist eine Alkylgruppe mit 1-6 Kohlenstoffatomen, b hat einen Wert von 2, 3 oder 4, p hat einen Wert von 0, 1 oder 2 und Q ist ein Wasserstoffatom oder ein Rest der Formel - CHR²CHR³COOR⁴, in der R², R³ und R⁴ die zuvor angegebene Bedeutung haben, m einen Mittelwert von 40-600 hat und n einen Mittelwert von 0-100 hat, mit der Bedingung, daß, wenn n 0 ist, X die Bedeutung von Y hat und

(b) von 50-100 Gewichtsteile eines physiologisch verträglichen Trägers.

2. Haarbehandlungszusammensetzung nach Anspruch 1,

dadurch gekennzeichnet,

daß R Methyl ist und p den Wert von 1 aufweist.

3. Haarbehandlungszusammensetzung nach Anspruch 2, dadurch gekennzeichnet,

daß X Methyl ist, n einen Mittelwert von 1-100 aufweist und Y ein Substituent der Formel ist

 Haarbehandlungszusammensetzung nach Anspruch 3, dadurch gekennzeichnet,

daß das Polydiorganosiloxan die Formel aufweist

$$(\mathtt{CH_3})_3 \mathtt{Sio}(\mathtt{CH_3}_{\mathtt{Sio}})_n [(\mathtt{CH_3})_2 \mathtt{Sio}]_m \mathtt{Si}(\mathtt{CH_3})_3 \\ \mathtt{CH_2CH}(\mathtt{CH_3}) \mathtt{CH_2NCH_2CH_2CH_2CH_2COOR}^4 \\ \mathtt{Q} \qquad \mathtt{Q}$$

5. Haarbehandlungszusammensetzung nach Anspruch 4,

50 dadurch gekennzeichnet,

daß das Polydiorganosiloxan die Formel aufweist

- 6. Haarbehandlungszusammensetzung nach Anspruch 4,
 - dadurch gekennzeichnet,

daß etwa 50 % der Substituenten Q -CH₂CH₂COOR4 sind und der Rest Wasserstoff ist.

 Haarbehandlungszusammensetzung nach Anspruch 4, dadurch gekennzeichnet, daß das Polydiorganosiloxan die Formel aufweist

20 8. Haarbehandlungszusammensetzung nach Anspruch 4,

dadurch gekennzeichnet,

daß m einen Mittelwert von 40-400 hat, n einen Mittelwert von 1-60 hat und das Verhältnis von n zu m kleiner oder gleich 0,15 beträgt.

25 9. Haarbehandlungszusammensetzung nach Anspruch 8,

dadurch gekennzeichnet,

daß der Träger Wasser ist.

10. Haarbehandlungszusammensetzung nach Anspruch 1,

30 dadurch gekennzeichnet,

daß sie weiterhin von 2-40 Gewichtsteile eines oberflächenaktiven Spülmittels enthält, ausgewählt aus der Gruppe bestehend aus anionischen oberflächenaktiven Mitteln, nichtionischen oberflächenaktiven Mitteln und amphoteren oberflächenaktiven Mitteln.

11. Haarbehandlungszusammensetzung nach Anspruch 10,

dadurch gekennzeichnet,

daß das oberflächenaktive Spülmittel ein anionisches oberflächenaktives Mittel ist.

12. Haarbehandlungszusammensetzung nach Anspruch 11,

40 dadurch gekennzeichnet,

daß das anionische oberflächenaktive Mittel ein Natrium-, Ammonium- oder Triethanolaminsalz von Laurylsulfat ist.

- 13. Verfahren zum Konditionieren menschlichen Haares durch Inberührungbringen menschlichen Haares mit einer Zusammensetzung nach jedem der Ansprüche 1-12.
 - Verwendung einer Zusammensetzung nach jedem der Ansprüche 1-12 zum Behandeln menschlichen Haares.

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